Preparation and Reactions of Pyridones: Steric and Electronic Effects on Cycloadditions with 2(1*H*)-Pyridones

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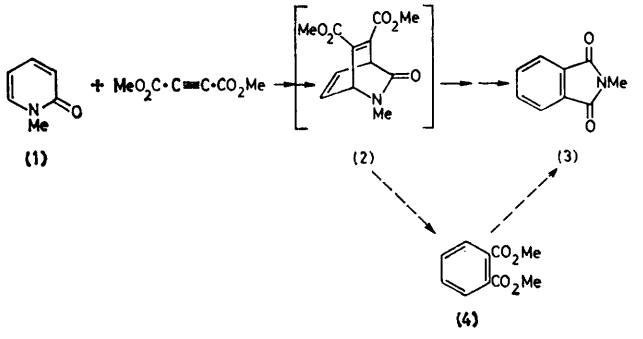
The reactions of a series of substituted 2(1*H*)-pyridones with dimethyl butynedioate have been studied. Cycloadditions across the 3,6-positions can be observed in certain instances and are particularly favoured where steric buttressing occurs between the substituent groups of the starting pyridones. The pyridone could not be induced to react with simple olefins, either by intermolecular or, *via* incorporation of alkenyl substituents, by intramolecular processes. From the results it is shown that 2-pyridones can be encouraged to behave as reactive classical dienes in cycloaddition reactions.

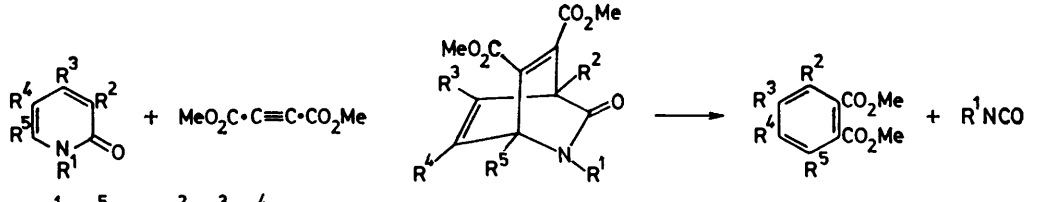
2(1*H*)-PYRIDONES have long attracted chemical attention for their hetero-aromatic character.[1] Studies, on their ability to sustain an induced ring current, led to estimates that they should possess only *ca.* 35% of the aromaticity of benzene, implying that the conjugated system should act as a diene in Diels-Alder type cycloaddition reactions.[2] An *X*-ray crystallographic study on 1-methyl-2-pyridone (1) supports this view, in that it is shown to contain carbon–carbon bonds which are alternately long and short.[3] However, early attempts to



SCHEME 1

illustrate such reactivity failed, partly owing to competing nucleophilic addition of the amide group to the dienophile.[4,5] Thus, ethoxyacetylene produces a mixture of *N*- and *O*-alkylated products.[6] Blocking of the nitrogen atom, by *N*-methylation, was more successful and it was found that dimethyl butynedioate added to the pyridone (1), under forcing conditions, to give a low yield of the phthalimide (3). Neither the postulated adduct (2) nor the product from consequential retro-Diels-Alder loss of methyl isocyanate, the phthalate (4) (Scheme 1), were detected.[7] Reaction between fumaronitrile and the pyridone (1) also proceeds in low yield,[8] as does addition of benzyne to a variety of dimethylpyridones.[9] More successful appears to be the addition of maleimide and *N*-substituted maleimides, which produce mixtures of *endo*- and *exo*-isomers in yields up to 40%.[10] Recently, the addition of fumaric acid to (1) has been described,[11] whilst 4-phenyl-1,2,4-triazoline-3,5-dione produces an 80% yield of the corresponding cycloadduct.[12] It appears that the pyridone component undergoes cycloaddition more smoothly when a conjugating vinyl group is placed on the nitrogen atom.[13]

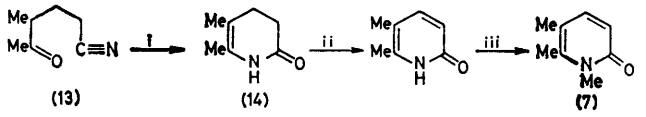
Our studies [14] on pyridones commenced from previous observations that various pyrimidones and pyrazinones [15] readily participated in cycloadditions. It was of interest to compare the reactivity of a series of substituted pyridones. The pyridones used in these studies (Scheme 2) were generally obtained by standard methods. The 2-pyridones (5) and (6) were synthesized by diazotisation and subsequent hydrolysis of the corresponding 2-



(5) $R^1 = R^5 = Me$, $R^2 = R^3 = R^4 = H$	(16)	(21)
(6) $R^1 = R^2 = Me$, $R^3 = R^4 = R^5 = H$	–	(21)
(7) $R^1 = R^4 = R^5 = Me$, $R^2 = R^3 = H$	(17)	
(8) $R^1 = Me$, $R^2 = R^3 = R^4 = H$, $R^5 = OMe$	–	(22)
(9) $R^1 = Me$, $R^2 = R^4 = R^5 = H$, $R^3 = Ph$	(18)	(23)
(10) $R^1 = R^5 = Me$, $R^2 = R^4 = H$, $R^3 = Ph$	(19)	(24)
(11) $R^1 = R^3 = R^5 = Me$, $R^2 = R^4 = H$	(15)	(25)
(12) $R^1 = OMe$, $R^2 = R^4 = H$, $R^3 = R^5 = Me$	(20)	(25)

SCHEME 2

aminopicolines, followed by *N*-methylation.[16] The new trimethylpyridone (7) was prepared by initial cyclisation of 3-acetylvaleronitrile (13) over neutral alumina, followed by oxidation with sulphuryl chloride, to give the dimethylpyridone (14), followed by *N*-methylation



SCHEME 3 *Reagents:* i, Al_2O_3; ii, SO_2Cl_2; iii, MeI, NaOEt

(Scheme 3). 6-Methoxy-1-methyl-2-pyridone (8) was generated by thermal rearrangement of 2,6-dimethoxypyridine in methyl iodide. The 4-phenyl-substituted-pyridones were prepared by established methods, pyridone (9) being obtained by ferricyanide oxidation of 1-methyl-4-phenylpyridinium methosulphate, and pyridine (10) from benzoylacetonitrile by the method of Hauser *et al.*[17]

The reaction of the pyridones with dimethyl butynedioate gave the results listed in Table 1. In order

TABLE 1 [a]

Pyridone	% Reaction [b]	Product	% Isolated yield
(5)	22	(16)	20
(6)	0		0
(7)	75	(17)	71
(8)	0		0
(9)	0 [c]	(18)	0 (36)
(10)	73	(19)	70
(11)	(31) [d]	(15)	31
(12)	0 [d,e]	(20)	0 (8)

[a] Solutions were approximately 1.6M in pyridone. [b] Yield by ^{1}H n.m.r. monitoring of disappearance of the starting *N*-methyl signal against appearance of product. [c] Traces were detected; reaction in neat dimethyl butynedioate gave the adduct (28) in 36% yield. [d] From the work of Heep (ref. 18); corrected yield quoted for (15). [e] Traces were detected. Reaction under the standard condition for 170 h gave the adduct (20) in 8% yield.

to assess relative reactivities of these variously substituted compounds a standard set of reaction conditions was chosen; attempts to quantify reaction rates were thwarted by the wide variation in reaction rates between the various pyridones, the thermal instability of the acetylenic ester and the tendency, in some instances, for the initial bicyclic adducts, *e.g.* (2), to fragment to the corresponding phthalate. The conditions used, degassed solutions of the pyridone in acetonitrile containing 1.1 equivalents of the acetylenic ester, heated at 80 °C for 72 h, were originally employed by Heep,[18] who had shown that the trimethylpyridone (11) reacted under these conditions to give the bicyclic adduct (15) whilst the *N*-methoxypyridone (12) only reacted sluggishly to give the adduct (20). Reactions were monitored by disappearance of the *N*-methyl signal of the starting material in the ^{1}H n.m.r. spectrum. Under these standard conditions the isolated products were mainly the corresponding bicyclic adducts (Table 1) although more vigorous conditions, *e.g.* 140 °C for 14 h gave the phthalate ester arising from the retro-Diels-Alder process (Scheme 2, Table 2). Full details are presented in the Experimental section.

Molecular orbital calculations clearly show [19] that the dominant orbital interaction in the addition step will be between the highest occupied molecular orbital of the 2-pyridone and the lowest unoccupied molecular orbital of the acetylenic ester, *i.e.* that a classical type of cycloaddition will be operating.[20] A comparison of the results tabulated for the methyl-substituted pyridones (5), (6), (7), and (11) shows that substitution into position 6 has

TABLE 2

Pyridone	Conditions [a]	Product	Isolated yield (%)
(5)	145 °C; 14 h	(21)	87
(6)	145 °C; 14 h	(21)	21
(8)	145 °C; 14 h	(22)	96
(9)	140—145 °C; 110 h [b,c]	(23)	75
(10)	145 °C; 14 h [b]	(24)	89

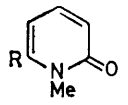
[a] Pyridones were heated in an excess of neat dimethyl butynedioate under degassed conditions in sealed glass tubes. [b] The pyridone was dissolved in a few drops of acetonitrile before an excess of the ester was added. [c] Fresh dimethyl-butynedioate was added after 14 h before heating of the solution was continued for the extended time.

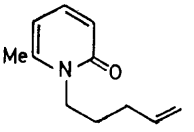
the greatest effect on the rate of cycloaddition. That this is primarily a steric rather than an electronic effect is supported by a comparison of the results for the pyridones (7) and (11). In the former case the 6-methyl group is buttressed against both the 1- and the 5-methyl groups. When the same groups are spatially separated, as in (11), the rate of the cycloaddition is substantially decreased. A comparison of (8) with (5) shows a consistent trend. If the electronic influence was of primary importance at the 6-position one would expect, for a classical type of Diels-Alder process, the rate of addition to be greater for (8). The reverse is observed and, since the methyl group is bulkier, with respect to its buttressing effect, than a methoxy-group,[21] a steric effect is again implied. The same argument also applies to the conjugated pyridone (9), which gives only traces of the adduct (18) under the standard conditions, although a combination of both steric and electronic effects, as in (10), does show a significant rate enhancement. Indeed the phenyl-substituted pyridone (10) appears to be a substantially better diene than its methyl analogue (11), indicating that, for (10), the electronic effect of the phenyl group is of importance.[22]

After this work had been completed it was reported that, as expected, use of high pressures will also aid the cycloaddition step.[23]

The net effect of the buttressing of methyl substituents is to impart strain to the pyridone ring, raising the energy of its highest occupied molecular orbital.[19] Cycloaddition across the 3,6-positions helps to relieve this strain, as the reaction sites rehybridise from sp^2 to sp^3, the activation energy for the process being lowered. A similar buttressing effect has been noted for cycloadditions across anthracenes,[24,25] and isoquinolinium salts and related systems.[26] It is likely to be a very general effect.

The relative sluggishness of the above cycloaddition reactions, together with those reported in the literature, and the observation that simple olefins, *e.g.* cyclopentene, did not react with these systems suggest that they behave as classical dienes tending to the neutral demand type.[20] Attempts to encourage cycloaddition to olefins by use of intramolecular reactions failed. For example, the substituted pyridones (26), (27), and (28) were prepared but none underwent cycloaddition at temperatures up to 250 °C; above this temperature general





(26) R = $[CH_2]_4CH{=}CH_2$

(27) R = $[CH_2]_4C{\equiv}C{\cdot}SiMe_3$

(28)

decomposition processes set in. It would be of interest to examine the effect of high pressure on such substrates since this should reinforce the favourable entropy factor between the intramolecularly bound reactants.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 157G spectrometer on solutions in chloroform unless otherwise stated. ^1H N.m.r. spectra were recorded on a Jeol MH-100 instrument using deuteriochloroform solutions with tetramethylsilane as internal reference (s, singlet; d, doublet; t, triplet; q, quartet; dd, double doublet; m, multiplet). Mass spectral measurements were performed on an A.E.I. MS30 or MS50 instrument. Solvents were generally distilled before use. Acetonitrile was dried by distillation from calcium hydride and stored over 4 Å molecular sieves. Chromatography was carried out on Merck Kieselgel GF_{254} and visualised with either u.v. light or iodine. Thermolyses were carried out in sealed tubes after degassing by freezing in liquid nitrogen and evacuating the tube using a ' freeze-thaw ' cycle. Sealed tubes and contents were heated in stills containing refluxing solvents of appropriate boiling points.

General Method for N-*Methylation of* 2(1H)-*Pyridones*.[16]—One equivalent of sodium ethoxide, prepared by dissolving the appropriate amount of sodium in freshly distilled ethanol, was added to a solution of the pyridone in dry ethanol. After the solution had been stirred for 2 h the solvent was evaporated off and the residue dissolved in dry dimethylformamide. Methyl iodide (1.1 equiv.) was added to the solution which was then stirred for 18 h at room temperature before being poured into water and extracted into dichloromethane (×3). The organic extract was dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Where necessary the product was purified by SiO_2 column chromatography using ethyl acetate–light petroleum (b.p. 60—80 °C) mixtures as eluant.

1,6-*Dimethyl*-4-*phenyl*-2(1H)-*pyridone* (10).—6-Methyl-4-phenyl-2(1*H*)-pyridone [17] (1.01 g), methylated by the general procedure, gave, after recrystallisation from ether, the *title compound* (10), as a pale yellow solid, m.p. 106—107 °C, $\nu_{max.}$ 3 000, 1 660, 1 570, and 1 360 cm^{-1}; δ 7.60—7.30 (5 H, m), 6.60br (1 H, s), 6.20br (1 H, s), 3.48 (3 H, s), and 2.32 (3 H, s) (Found: C, 78.7; H, 6.4; N, 6.8. $C_{13}H_{13}NO$ requires C, 78.4; H, 6.6; N, 7.0%).

1,5,6-*Trimethyl*-2(1H)-*pyridone* (7).—Ethyl methyl ketone (72 g) was stirred with a methanolic solution of potassium hydroxide (0.5 g in 1.5 ml) for 15 min at 0 °C before acrylonitrile (30 g) in tetrahydrofuran (50 ml) was added as drops during 20 min, the temperature being kept below 15 °C. The yellow solution was stirred for a further 1 h at this temperature before being neutralised to pH 7 with conc. HCl. Water (5 ml) was added and the organic phase collected and the excess of solvent evaporated off before distillation of the residue, to afford 3-acetylvaleronitrile (13) (29 g, 41%), b.p. 98—102 °C/5 mmHg (lit.,[27] b.p. 114—115 °C/15 mmHg).

The valeronitrile (9.0 g) was added to activated neutral alumina (4.5 g) and the slurry sealed in a Pyrex tube under reduced pressure before being heated at 200 °C for 2 h and then at 220 °C for a further 3 h. After cooling, the tube was opened, the residue washed with benzene and the benzene extracts evaporated *in vacuo* to yield 3,4-dihydro-5,6-dimethyl-2(1*H*)-pyridone (7.9 g, 87%) as a yellow, crystalline solid, m.p. (benzene) 128—129 °C (lit.,[28] m.p. 130 °C).

To a stirred solution of 3,4-dihydro-5,6-dimethyl-2(1*H*)-pyridone (2.0 g) in chloroform (30 ml) at 50 °C was added, dropwise, a solution of sulphuryl chloride (2.16 g) in chloroform (10 ml). After 30 min the solvent was evaporated and the residue heated for 0.5 h at 120 °C. The cooled mixture was diluted with water (20 ml) and neutralised with ammonia (*d* 0.88) to precipitate 5,6-dimethyl-2(1*H*)-pyridone (14) (0.9 g, 45%), m.p. (H_2O) 205—207 °C (lit.,[28] m.p. 206—207 °C). Methylation of the pyridone (14) by the general method afforded the *pyridone* (7) (60%), as an air-sensitive pale yellow compound, m.p. (ethyl acetate) 84—85 °C, $\nu_{max.}$ 3 020, 1 675, 1 600, 1 540, 1 170, 1 115, 970, and 910 cm^{-1}; δ 7.00 (1 H, d, *J* 8 Hz), 6.32 (1 H, d, *J* 8 Hz), 3.50 (3 H, s), 2.22 (3 H, s), and 2.02 (3 H, s) (Found: M^+ 137.0846. $C_8H_{11}NO$ requires M^+ 137.0841).

1-*Methyl*-4-*phenyl*-2(1H)-*pyridone* (9).—4-Phenylpyridine (2.85 g) in acetonitrile (20 ml) was heated with dimethyl sulphate (2.31 g) at reflux for 14 h. The solution was evaporated to dryness under reduced pressure to produce the methosulphate salt as pink crystals. The crude salt was dissolved in water and this was added dropwise, together with, but separately from, an aqueous solution of 2N-sodium hydroxide (1 equiv.), to a stirred solution of potassium ferricyanide (13.7 g) in water (30 ml) cooled in an ice–water bath. Addition took 30 min, and the mixture was then stirred for a further 4 h at ambient temperature before the mixture was filtered. The aqueous phase and filtrate were extracted with dichloromethane (×3), and the organic extract dried and evaporated to give the *title pyridone* (2.4 g, 71%), m.p. 139—141 °C, $\nu_{max.}$ 2 965, 1 656, 1 588, 1 580, 1 408, 1 341, and 869 cm^{-1}; δ 7.39—7.75 (6 H, m), 6.87 (1 H, d, *J* 2 Hz), 6.48 (1 H, dd, *J* 2, 7 Hz), and 3.60 (3 H, s) (Found: M^+ 185.0841. $C_{12}H_{11}NO$ requires M^+ 185.0841).

1,3-*Dimethyl*-2(1H)-*pyridone* [29] (6).—This compound was obtained as a colourless oil, b.p. 93 °C/2 mmHg (lit.,[29] b.p. 78 °C/0.5 mmHg).

1,6-*Dimethyl*-2(1H)-*pyridone* [29] (5).—This compound was obtained as a deliquescent white solid, m.p. 55—57 °C (lit.,[30] m.p. 55—58 °C).

6-*Methoxy*-1-*methyl*-2(1H)-*pyridone* (8).—This compound was obtained as a white crystalline compound, m.p. 52—56 °C (lit.,[31] m.p. 52—54 °C).

Thermolyses of N-*Methyl*-2(1H)-*pyridones with Dimethyl Butynedioate*.—All thermolyses were carried out under reduced pressure in sealed Pyrex tubes as degassed solutions in acetonitrile containing 1.1 equiv. of dimethyl butynedioate. In each case the volume of the solution was adjusted with acetonitrile so that it became *ca.* 1.6M with respect to the pyridone at room temperature. The sealed tubes were placed in refluxing stills of benzene or xylene, as appropriate, after which time the glass phials were rapidly cooled and the contents removed. The acetonitrile was removed under reduced pressure and the crude mixture examined by ^{1}H n.m.r. spectroscopy. Products were isolated by preparative t.l.c. as detailed below.

Dimethyl 1,2-*Dimethyl*-3-*oxo*-2-*azabicyclo*[2.2.2]*octa*-5,7-*diene*-7,8-*dicarboxylate* (16).—1,6-Dimethyl-2(1*H*)-pyridone (5) (48 mg) was treated with the acetylenic ester (84 mg) in acetonitrile at 80 °C for 72 h to give, by preparative t.l.c., the *title compound* (21.5 mg, 20%), m.p. (ethyl acetate) 88—89 °C, $\nu_{max.}$ 2 940, 1 735, 1 720, 1 680, 1 648, 1 435, 1 370, 1 320, 1 120, 1 090, 940, and 910 cm^{-1}; δ 6.97 (1 H, dd, *J*, 7, 7 Hz), 6.49 (1 H, dd, *J* 2, 7 Hz), 4.89 (1 H, dd, *J* 2, 7 Hz), 3.88 (3 H, s), 3.80 (3 H, s), 2.80 (3 H, s), and 1.82 (3 H, s) (Found: M^+ 265.1001. $C_{13}H_{15}NO_5$ requires M^+ 265.1005).

Dimethyl 1,2,6-*Trimethyl*-3-*oxo*-2-*azabicyclo*[2.2.2]*octa*-5,7-*diene*-7,8-*dicarboxylate* (17).—1,5,6-Trimethyl-2(1*H*)-pyridone (7) (151 mg) with dimethyl butynedioate (200 mg) in acetonitrile at 80 °C for 72 h gave, by preparative t.l.c. the *title compound* (213 mg, 71%) as a white solid, m.p. [ethyl acetate–light petroleum (b.p. 60—80 °C)], 79—81 °C, $\nu_{max.}$ 2 930, 1 720, 1 670, 1 650, 1 635, 1 430, 1 380, 1 320, and 1 080 cm^{-1}; δ 6.41br (1 H, d, *J* 6 Hz), 4.62 (1 H, d, *J* 2 Hz), 3.80 (3 H, s), 3.72 (3 H, s), 2.80 (3 H, s), and 1.83 (3 H, d, *J* 2 Hz) (Found: M^+ 279.1092. $C_{14}H_{17}NO_5$ requires M^+ 279.1093).

Dimethyl 2-*Methyl*-3-*oxo*-5-*phenyl*-2-*azabicyclo*[2.2.2]*octa*-5,7-*diene*-7,8-*dicarboxylate* (18).—Only traces of this compound were formed under the standard conditions. 1-Methyl-4-phenyl-2(1*H*)-pyridone (9) (0.22 g) was heated in neat dimethyl butynedioate (2 ml) at 80 °C for 72 h. The excess of the ester was distilled off and the residue separated by preparative t.l.c. to yield the *title compound* (115 mg, 36%) as a pale yellow oil, $\nu_{max.}$ (film) 2 948, 2 845, 1 720, 1 685, 1 647, 1 434, 1 330, and 1 121 cm^{-1}; δ 7.32—7.61 (5 H, m), 6.98 (1 H, dd, *J* 2, 6 Hz), 5.30 (1 H, d, *J* 6 Hz), 5.20 (1 H, d, *J* 2 Hz), 3.90 (6 H, s), and 2.99 (3 H, s) (Found: M^+ 327.1077. $C_{18}H_{17}NO_5$ requires M^+ 327.1107).

Dimethyl 1,2-*Dimethyl*-3-*oxo*-5-*phenyl*-2-*aza*-*bicyclo*[2.2.2]-*octa*-5,7-*diene*-7,8-*dicarboxylate* (19).—The pyridone (10) (63 mg) was heated under the standard conditions with dimethyl butynedioate (76 mg) to give, after preparative t.l.c., the *title compound* (75.5 mg, 70%), as pale yellow crystals, m.p. (ether) 123—124 °C, $\nu_{max.}$ 2 930, 2 845, 1 735, 1 720, 1 685, 1 650, 1 430, 1 315, 1 130, 1 100, and 945 cm^{-1}; δ 7.60—7.24 (5 H, m), 6.58 (1 H, d, *J* 2 Hz), 5.38 (1 H, d, *J* 2 Hz), 3.90 (3 H, s), 3.84 (3 H, s), 2.88 (3 H, s), and 1.84 (3 H, s) (Found: M^+ 361.1364. $C_{19}H_{19}NO_5$ requires M^+ 341.1345).

Dimethyl 3-*Methylphthalate* (21).—The pyridone (6) (200 mg) when heated with neat dimethyl butynedioate (0.5 g) at 145 °C for 14 h gave, after isolation by preparative t.l.c., dimethyl 3-methylphthalate (21) (68 mg, 21%) as a colourless oil, δ 8.05—7.62 (1 H, m), 7.62—7.16 (2 H, m), 3.87 (6 H, s), and 2.30 (3 H, s).[32]

The same compound was produced, in 87% yield, from the thermolysis of the isomeric pyridone (5) in an excess of dimethyl butynedioate at 145 °C for 14 h.

Dimethyl 3-*Methoxyphthalate* (22).—The pyridone (8) (63 mg) when treated with an excess of neat dimethyl butynedioate at 145 °C for 14 h gave, after work-up by preparative t.l.c., the *phthalate* (96%) as white crystals, m.p. (ether) 75—79 °C (lit.,[33] m.p. 77 °C), $\nu_{max.}$ 1 727 and 1 588 cm^{-1}; δ 7.60—7.20 (2 H, m), 7.05 (1 H, dd, *J* 2, 10 Hz), 3.87 (3 H, s), 3.84 (3 H, s), and 3.82 (3 H, s).

Dimethyl 4-*Phenylphthalate* (23).—The pyridone (18) (0.18 g) was dissolved in acetonitrile (0.2 ml) and dimethyl butynedioate (0.16 g) was added to the solution before it was deoxygenated, sealed in a Pyrex tube, and heated to 140 °C for 14 h. ^{1}H N.m.r. analysis indicated incomplete reaction so the mixture was treated with a further equivalent of the ester and heated for 48 h at 145 °C; the latter process was repeated again before the mixture was worked up. Preparative t.l.c. afforded dimethyl 4-phenylphthalate (23)[34] (0.196 g, 75%) as a viscous oil, $\nu_{max.}$ (film) 3 050, 3 025, 2 994, 2 944, 1 721, 1 607, 1 431, 1 271, 1 128, 1 075, 962, 757, and 698 cm^{-1}; δ 7.41—8.03 (8 H, m) and 4.00 (6 H, s) (Found: M^+ 270.0900. Calc. for $C_{16}H_{14}O_4$: *M* 270.0892).

The phthalate ester (23) was also obtained following thermolysis of the adduct (28) for 48 h at 140 °C.

Dimethyl 3-*Methyl*-5-*phenylphthalate* (24).—The pyridone (19) (0.38 g) was dissolved in acetonitrile (0.2 ml) and dimethyl butynedioate (0.36 g) and the deoxygenated solution sealed in a Pyrex tube and thermolysed at 145 °C for 14 h. Work-up by preparative t.l.c. gave the *title compound* (0.48 g, 89%), as a pale yellow solid, m.p. (ether) 88—89 °C, $\nu_{max.}$ 3 030, 2 940, 1 735, 1 725, 1 610, 1 600, 1 330, and 1 105 cm^{-1}; δ 8.00br (1 H, s), 7.60—7.30 (6 H, m), 3.95 (3 H, s), 3.90 (3 H, s), and 2.40 (3 H, s) (Found: C, 72.1; H, 5.6. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5.7%).

6-*Hex*-5-*enyl*-1-*methyl*-2(1H)-*pyridone* (26).—1,6-Dimethyl-2(1*H*)-pyridone (4.03 g) and tetrahydrofuran (50 ml) at −23 °C were treated with butyl-lithium (2.10 g) in hexane under a nitrogen atmosphere for 1.5 h before 5-bromopent-1-ene (4.88 g) was added; the mixture was then stirred for 2 h at −23 °C before the temperature was allowed to rise to ambient. Water was added to the mixture which was then extracted with dichloromethane (3 × 20 ml); the organic extract was then dried. Repeated preparative t.l.c. afforded the *title pyridone* (0.41 g, 6.6%) as an oil, $\nu_{max.}$ (film) 3 063, 2 921, 2 856, 1 656, 1 647, 1 560, 1 432, 1 156, 910, and 793 cm^{-1}; δ 7.26 (1 H, dd, *J* 7, 9 Hz), 6.47 (1 H, d, *J* 10 Hz), 6.07 (1 H, d, *J* 7 Hz), 5.63—6.08 (1 H, m), 4.83—5.18 (2 H, m), 3.56 (3 H, s), 2.64 (2 H, t, *J* 7 Hz), 1.91—2.33 (2 H, m), and 1.41—1.84 (4 H, m) (Found: M^+ 191.1309. $C_{12}H_{17}NO$ requires M^+ 191.1310).

Thermolysis of samples of this pyridone, in acetonitrile or dimethylformamide, under degassed conditions at various temperatures, gave no changes up to 250 °C, above which extensive general decomposition set in.

1-*Methyl*-6-(6-*trimethylsilylhex*-5-*ynyl*)-2(1H)-*pyridone* (27).—6-Methyl-2(1*H*)-pyridone (1.6 g) in tetrahydrofuran (50 ml) at −23 °C under a nitrogen atmosphere was treated with butyl-lithium for 0.5 h before being cooled to −78 °C; 5-bromo-1-trimethylsilylpent-1-yne (3.60 g) was then added. After a further 0.5 h the solution was allowed to warm to room temperature before being quenched with water and extracted with dichloromethane (3 × 20 ml). Work-up, followed by preparative t.l.c., afforded 6-(6-*trimethylsilylhex*-5-*ynyl*)-2(1H)-*pyridone* (1.99 g, 49%) as white crystals, m.p. (ethyl acetate) 69 °C, $\nu_{max.}$ 2 920, 2 175, 1 660,

1 650, 1 620, and 1 544 cm^{-1}; δ 13.0br (1 H, s, exchangeable with D_2O), 7.35 (1 H, dd, *J* 7, 8 Hz), 6.45 (1 H, d, *J* 8 Hz), 6.08 (1 H, d, *J* 7 Hz), 2.66 (2 H, t, *J* 6 Hz), 2.26 (2 H, t, *J* 7 Hz), 1.98—1.46 (4 H, m), and 0.12 (9 H, s) (Found: C, 67.8; H, 8.55; N, 5.65. $C_{14}H_{21}NOSi$ requires C, 68.0; H, 8.55; N, 5.7%).

Methylation of this pyridone by the standard method afforded the *title pyridone*, isolated by preparative t.l.c. as a pale yellow oil, $\nu_{max.}$ (film) 2 950, 2 180, 1 660, 1 580, 1 500, 1 370, 1 240, 1 045, and 845 cm^{-1}; δ 7.20—6.88 (1 H, dd, *J* 7, 8 Hz), 6.16 (1 H, d, *J* 8 Hz), 5.90 (1 H, d, *J* 7 Hz), 3.44 (3 H, s), 2.68—2.48 (1 H, t, *J* 6 Hz), 2.32 (2 H, t, *J* 7 Hz), and 1.87—1.24 (4 H, m) (Found: M^+ 261.1432. $C_{15}H_{23}NOSi$ requires M^+ 261.1442).

Thermolysis of samples of this pyridone, either in acetonitrile or dimethylformamide, at temperatures up to 250 °C gave no observable products.

6-*Methyl*-1-*pent*-4-*enyl*-2(1H)-*pyridone* (28).—6-Methyl-2-(1*H*)-pyridone (3.0 g) was *N*-alkylated by the general method described above, using 5-bromopent-1-ene (4.1 g, 1.1 equiv.) in place of methyl iodide. Both *N*- and *O*-alkylated derivatives were formed. Thus, column chromatography (SiO_2), with ethyl acetate–light petroleum (b.p. 60—80 °C) as eluant, afforded, initially, 6-methyl-2-pent-4-enyloxypyridine (3.0 g, 62%) as a pale yellow oil. After purification by preparative t.l.c., this showed $\nu_{max.}$ (film) 3 070, 2 942, 1 641, 1 599, 1 578, 1 449, 1 307, 1 234, and 790 cm^{-1}; δ 7.28 (1 H, t, *J* 7 Hz), 6.40—6.64 (2 H, m), 5.58—6.04 (1 H, m), 4.87—5.13 (2 H, m), 4.29 (2 H, t, *J* 7 Hz), 2.39 (3 H, s), 2.06—2.28 (2 H, m), and 1.71—1.97 (2 H, m) (Found: M^+ 177.1153).

The second product eluted was the *title pyridone* (28) (1.049 g, 10%), isolated as an oil, $\nu_{max.}$ 2 963, 2 920, 2 882, 1 657, 1 570, 1 552, 1 436, 1 411, 1 178, 992, and 914 cm^{-1}; δ 6.92—7.12 (1 H, m), 6.24 (1 H, d, *J* 8 Hz), 5.51—5.98 (2 H, m), 4.79—5.11 (2 H, m), 3.91 (2 H, t, *J* 8 Hz), 2.36 (3 H, s), 1.95—2.26 (2 H, m), and 1.54—1.93 (2 H, m) (Found: M^+ 177.1152. $C_{11}H_{15}NO$ requires M^+ 177.1153).

Heating samples of the *N*-alkylated pyridone (28) in acetonitrile gave no cycloadducts at temperatures up to 250 °C.

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